CARBON MATERIALS RESEARCH
TASK 2306BPB3

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Abstract

Carbon-carbon composites have been used by the Air Force and others for over 25 years in a variety of thermostructural applications including rocket propulsion, re-entry, hypersonics and aircraft brakes. Although the technology is mature, these materials are still very expensive, have long lead-times, are limited in thickness, are not uniform in density, and cannot be used in an oxidizing environment for extended periods without some type of protection. There is currently no commercial process that can meet Phase 3 IHPRPT cost and schedule goals for nozzles and exit cones.

Research Objective

To develop a new densification process that will address all the processing shortcomings mentioned above, that are still extant in carbon-carbon composites. This process should be based on a more fundamental understanding of carbon-carbon composites and of the shortcomings of current densification processes.

An extensive and in-depth understanding of the deficiencies of both the infiltration and impregnation densification processes currently employed by the industry, has led to the conception and implementation of a radically different densification process. This liquid phase approach addresses the main issue of wettability of the carbon precursor and its relationship to molecular weight and char yield. This issue has been overlooked and ignored by both the scientific community and the industry in the more than 25 year history of carbon-carbon composites.

The approach used to rectify the shortcomings of carbon-carbon composites mentioned above is to use an In Situ Densification process in which the fiber preform is impregnated with a low-molecular-weight form of the carbon matrix precursor rather than the precursor itself. This means that a low-molecular-weight material that not only has low viscosity but also wets the preform can be used for complete impregnation of the preform. This impregnant can then be thermally processed *in situ* to produce a high-molecular-weight, high viscosity material with a high char yield.

Progress

Since wettability of the impregnant is one of the associated features of the process that allows dramatic improvements in material properties, as well as reduction in costs and time,

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
14 JUL 2005		**-**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Carbon Materials Research	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
Wesley Hoffman	**2306**
	5e. TASK NUMBER **0529**
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
Air Force Research Laboratory (AFMC),AFRL/PRSM,10 E. Saturn Blvd.,Edwards AFB,CA,93524-7680	

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Carbon-carbon composites have been used by the Air Force and others for over 25 years in a variety of thermostructural applications including rocket propulsion, re-entry, hypersonics and aircraft brakes. Although the technology is mature, these materials are still very expensive, have long lead-times, are limited in thickness, are not uniform in density, and cannot be used in an oxidizing environment for extended periods without some type of protection. There is currently no commercial process that can meet Phase 3 IHPRPT cost and schedule goals for nozzles and exit cones.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**		**6**	

significant effort has gone into understanding this phenomenon. We continue to work with Professor Robert Hurt of Brown University to better understand and model this behavior. Prior to working with our group, Professor Hurt had done work in modeling the interactions of carbonaceous mesophase pitch with various surfaces. Under funding from our group, this work is being extended to numerous carbonaceous surfaces. He is looking at the wetting behavior, interfacial energies, and surface molecular orientation (surface anchoring states) for mesophase pitch on carbon fibers and other substrates. In addition, he is developing a theory/model to explain the unusual behavior of this liquid crystalline system. This work is important in understanding how to get the impregnant into the preform, how to enhance the impregnation, how to align the discotic liquid crystalline mesophase, and how to keep the mesophase in the preform during conversion to a carbon matrix.

Another important aspect of our research is gaining insight into the mechanism of the conversion of polynuclear aromatic compounds into carbonaceous mesophase. To this end, we continue a cooperation with Dr. Bahram Fathollahi and Professor Pao Chau of the University of California at San Diego. They are principally employing polarized light microscopy to observe the conversion to mesophase, to characterize the partially densified composites, as well as determine the structure of the high quality carbon matrix formed by this process.

A very significant amount of time and effort again this year has been involved in modifying, procuring components for, and fabricating an instrumented research reactor to study the In Situ Densification Process in a very controlled manner. This reactor has the ability to operate at temperatures as high as 650^{o}C and pressures up to 100 pounds/in^{2} (0.69 MPa). The reactor chamber volume can be as small as 15 cubic centimeters or as large as 225 cubic centimeters. The entire system, including data logging, is controlled by a computer providing hands-off operation. A cold trap capable of operating at temperatures as low as -40^{o}C is located between the reactor chamber exit port and the solenoid valves that direct any reactor effluent to one or more of three destinations. The first of these is simply a vent to a hood or other collection device. The second routes gases exiting the cold trap to a mass spectrometer. A pressure let-down system using 1 cm^{3} and 1000 cm^{3} holding tanks reduces pressure at the mass spectrometer sampling port to 5 Torr. The placement of the cold trap ensures that all condensables in the reactor effluent are removed before contamination of pressure transducers, solenoid control valves, and/or the over-pressure safety rupture disk can take place. Moreover, the cold trap itself is fitted with a sampling port that lets a pipette remove any liquid captured in the cold trap. In this fashion, cold trap contents can be segregated during an experiment without taking apart the reactor system. A manual ball valve lets the reactor chamber be isolated from the cold trap for long enough period of time to obtain a cold-trap sample.

The versatility of this mini-reactor system allows it to be used for a variety of research projects. However, its primary goal is to employ it for the study of polymerization and pyrolysis reactions occurring in hydrocarbons used in the fabrication of carbon fibers, foams, and carbon-carbon composites that are vital to the mission of the United States Air Force. The mini-reactor system has already provided data previously unknown about the fabrication of carbon-carbon composites using AFRL's patented In-Situ Densification Process. These

data include the role of the catalyst, precursor, and the reactor wall on the reaction products as well as the effect of vacuum, pressure, preform type and density, and particulate loading on pore-filling efficiency.

It was reported last year that an endotherm has been observed in the reactor. The following graph (Figure 2) illustrates the temperature profiles obtained in a densification experiment.

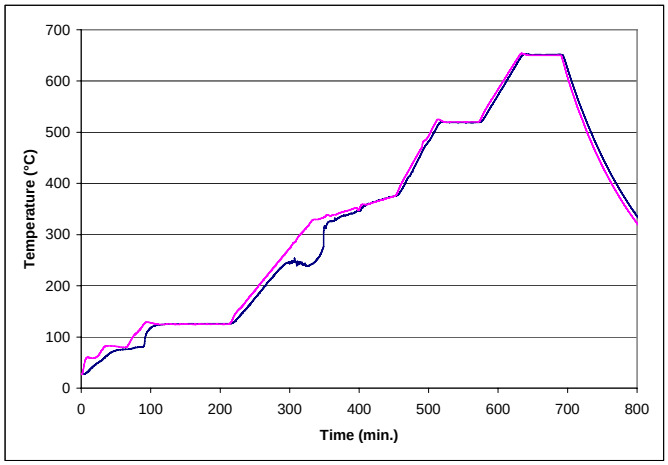

Figure 2: Trace of heater (light line) and sample (dark line) temperature.

The light line indicates the temperature of the external reactor wall, which is controlled quite accurately by the computer. The darker line is the temperature of matrix material used in the In-Situ Densification Process. The thermocouple used for this measurement is located directly on top of the carbon-fiber preform within the reactor chamber. Such precise placement of thermocouples was previously not possible. As can easily be observed between the temperatures of 250^{o}C and 325^{o}C, the matrix material undergoes some sort of endothermic process which was not known before this study. Further experiments have revealed that the temperatures between which this endothermic process are observed are a function of the heat-up rate. In addition, it has been observed that soaking in the temperature range 200-270°C made the endotherm more pronounced and showed that there are two different processes responsible for the endotherm. The process responsible for the lower temperature (250-275°C) portion of the endotherm is eliminated by increasing the pressure. The higher temperature portion of the endotherm is associated with the pressure vent a ~315°C. Neither process is associated with liquid evaporation but rather to decomposition reactions which produce the cold-trap liquids. These are primarily species such as tetralin, toluene, cyclohexane, and benzene but the product mixture may contain up to 100 constituents.

It has long been known that poly-aromatic hydrocarbons (PAH's) such as naphthalene and anthracene can be caused to undergo addition reactions and ring-closure reactions at low temperatures in the presence of strong Lewis acids, such as aluminum chloride and boron trifluoride. However, Scholl (1) reported in 1912 that even less strong acids such as anhydrous copper chloride and anhydrous ferric chloride also promote such reactions with PAH's. This line of research was primarily part of mainstream organic chemistry until Mochida (2) extended it to the production of mesophase pitch by dramatically raising

reaction temperatures. He started with 1-methylnaphthalene and using a mixture of boron tri-fluoride and hydrogen fluoride as the Lewis acid, obtained a black, tarry solid. This would previously have been dismissed as a bad end result by chemists because of the analytical difficulties involved i.e. it is a very insoluble material. Mochida, however, recognized that this material was liquid-crystalline mesophase pitch, which was discovered by Brooks and Taylor (3) in 1965. His primary goal was the production of carbon fibers from this mesophase pitch. Mochida did attempt at one point to use mesophase pitch as a binder for carbon-carbon composites. But, he still performed the reaction outside of the carbon-fiber preform thereby incurring the shortcomings of all pitch-based processes: the inability to easily and uniformly infiltrate the carbon-fiber preform as well as the need for stabilization. The patented In-Situ process sidesteps these shortcomings by deliberately infiltrating the carbon-fiber preform with one of several possible PAH's and a Lewis acid catalyst, and then forming mesophase pitch inside the preform itself.

We use naphthalene with $AlCl_3$ in our standard process. The choice is based on performance, cost, availability and ease of use. On the basis of the literature, we have investigated the use of other precursors and catalysts. In addition, we have investigated the catalytic effect of the reactor wall itself.

In order to see the effect of the reactor wall, our reactor was modified to accept inserts of different materials including aluminum, quartz, nickel and iron. Nickel and iron were chosen because they are major components of the 316 stainless steel used in our standard reactor while aluminum was selected because of our catalyst. It was found that the reactor wall affected the presence of the endotherm, the amount of liquid and gaseous products, as well as the type of solid product produced. It was found that the SS reactor was superior to the other materials.

On the basis of the Schole reaction, other Lewis acids (chlorides of copper, iron, and nickel) were tried, usually in combination with $AlCl_3$, to see if there was any enhanced catalytic effect. With each of these catalysts used in conjunction with the normal amount of $AlCl_3$ and at half the concentration of $AlCl_3$, there were similar effects on the reaction. In each case, in contrast to $AlCl_3$ alone, there were no liquid products and no venting of gas phase products. This means that none of these mixtures was catalytic for pyrolysis reactions. In contrast to the catalyst mixtures, when copper chloride was utilized by itself, it appeared to be a de-polymerization catalyst producing greatly increased venting.

Although naphthalene works well as a mesophase precursor, it is not the only polynuclear aromatic molecule that can be used to produce a high quality carbon matrix and may not be the best. To this end several other mesophase precursors were utilized both singly and in combination with other molecules. The precursors studied included naphthalene, 1-methylnaphthalene, 2- methylnaphthalene, anthracene, and acenaphthene. These precursors were selected on the basis of cost, structure, and availability.

In particular, acenaphthene, which has the structure of naphthalene with an ethylene bridge between the #1 and # 8 positions on the naphthalene aromatic double ring, was chosen because it was thought that this bridge would increase the likelihood of bond formation in the

presence of a Lewis acid catalyst, such as anhydrous aluminum chloride. Evidently, acenaphthene is able to easily interact with other poly-aromatic hydrocarbons in the presence of anhydrous aluminum chloride, which is what was expected theoretically. However, this leads to more small fragmentary hydrocarbons instead of building larger poly-aromatic molecules as hoped. The conclusion to be drawn from this sequence of experiments is that acenaphthene addition at a 50%-50% molar ratio does not enhance char yield and weight uptake for feedstocks that already have high densification efficiency, only helping when that efficiency is low to begin with.

Although there are differences among the various precursors, the main conclusion that can be drawn from this aspect of our studies is that the various precursors behave remarkably similarly while exhibiting minor differences in char yield and product distribution. There are much larger differences that result from preform composition and density.

In normal carbon fiber preform impregnation, vacuum is used to help get the viscous non-wetting matrix precursor into the preform while pressure is used to hinder the egress of volatile carbonization products in order to increase char yield. With the advantages of the In Situ process, it was anticipated that both pressure and vacuum would have less beneficial effect than with conventional processing. This proved to be the case.

Pulling a vacuum on the preform and then introducing molten naphthalene/$AlCl_3$ did not work as the molten material blocked the transfer tube. However, if the sample was covered with naphthalene/$AlCl_3$ powder, evacuated, and then heated, there was a measurable increase in weight uptake especially on the second densification cycle. There was also a measurable increase in weight uptake by raising the pressure in the reactor during carbonization to 95 psi. In addition, the increased pressure forced the liquid pyrolysis products, which usually amount to ~10% of the feedstock, to stay in the reactor.

References

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Acknowledgement/Disclaimer

This work was supported (in part) by the Air Force Office of Scientific Research, USAF. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the Air Force Office of Scientific Research or the U.S. Government.

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Publications

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K. M. Chioujones, W. Ho, P. C. Chau, B. Fathollahi, P. G. Wapner, and W. P. Hoffman, "Microstructural Studies of In-Situ Mesophase Transformation in the Fabrication of Carbon-Carbon Composites", Accepted by Carbon

US Patent 6818162 "Method of Manufacture of Baby-Feeding Nipple" W.P. Hoffman, P.G. Wapner, and A. Pechenik (16 November 2004)

U S Patent 6,867,854 "Liquid To Solid Angle of Contact Measurement" P.G. Wapner and W.P. Hoffman (March 15, 2005) Both these patents issued w/o any changes!

Patents Filed:

Four disclosures were filed.

Awards Received

Dr. Wes Hoffman was elected as Chairman of the Executive Committee of the American Carbon Society.

Transitions

The In Situ Densification technology developed in this research is being incorporated through a CRADA with SMJ Carbon Technology into Air Force programs.